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(21) International Application Number: PCT/US99/18708 (22) International Filing Date: 18 August 1999 (18.08.99) (30) Priority Data: 60/096,942 18 August 1998 (18.08.98) US (71) Applicants (for all designated States except US): E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL [-/US]; Office of Technology Development, CB#4105, 308 Bynum Hall, Chapel Hill, NC 27599-4105 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): SVEJDA, Steven, Arthur [US/US]; 4600 Highgate Drive, Durham, NC 27713 (US). (74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: MANUFACTURE OF α -OLEFINS (57) Abstract In the oligomerization of ethylene to linear α -olefins using selected nickel complexes of α -diimines, the use of dialkylaluminum chlorides as the cocatalysts allows a distribution containing a larger proportion of higher α -olefins to be made (higher Schulz-Flory constant).		

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TITLEMANUFACTURE OF α -OLEFINSFIELD OF THE INVENTION

In the preparation of linear α -olefins by the
5 oligomerization of ethylene and using catalyst systems
containing nickel complexes of certain α -diimines, the
Schulz-Flory constant of the product distribution may
be raised by using dialkyl aluminum halides as
cocatalysts.

10 TECHNICAL BACKGROUND

Linear α -olefins, especially those containing
about 6 to about 20 carbon atoms, are important items
of commerce, with about 1.5 million tons reportedly
being produced in 1992. The α -olefins are used as
15 intermediates in the manufacture of detergents, as
monomers (especially in linear low density
polyethylene), and as intermediates for many other
types of products. As a consequence, improved methods
of making these compounds are of interest.

20 Most commercially produced α -olefins are made by
the oligomerization of ethylene, catalyzed by various
types of compounds, see for instance B. Elvers, et al.,
Ed. Ullmann's Encyclopedia of Industrial Chemistry,
Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989,
25 p. 243-247 and 275-276, and B. Cornils, et al., Ed.,
Applied Homogeneous Catalysis with Organometallic
Compounds, A Comprehensive Handbook, Vol. 1, VCH
Verlagsgesellschaft mbH, Weinheim, 1996, p. 245-258.
The major types of commercially used catalysts are
30 alkylaluminum compounds, certain nickel-phosphine
complexes, and a titanium halide with a Lewis acid such
as AlCl_3 . However improved catalysts for making such
olefins are of constant interest.

World Patent Application 96/23010 describes the
35 use of certain α -diimine nickel complexes, and

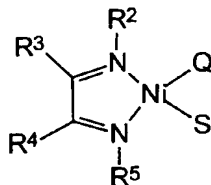
cocatalysts such as alkyl aluminum compounds, for the oligomerization of ethylene to linear α -olefins. The effect of dialkyl aluminum halides on the Schulz-Flory distribution of the resulting product is not disclosed.

5 SUMMARY OF THE INVENTION

This invention concerns a process for the production of α -olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$:

ethylene;

- 10 a first compound W of the formula $\text{R}^6\text{R}^7\text{AlY}$; and
a second compound of the formula



(I)

wherein:

- 15 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted

- 20 hydrocarbylene to form a ring;

R^6 and R^7 are each independently alkyl;

Y is chlorine or bromine; and

Q and S are each independently an anion;

- and wherein an α -olefin containing 4 to 40 carbon
25 atoms is produced.

DETAILS OF THE INVENTION

Herein certain terms are used to define certain chemical groups or compounds. These terms are defined below.

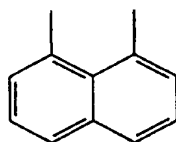
- 30 • A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise

stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

• By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more
5 substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not
10 otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.

• By an alkyl aluminum compound is meant a compound in which at least one alkyl group is bound to
15 an aluminum atom. Other groups such as alkoxide, oxygen, and halogen may also be bound to aluminum atoms in the compound.

• By "hydrocarbylene" herein is meant a divalent group containing only carbon and hydrogen.
20 Typical hydrocarbylene groups are $-(CH_2)_4-$, $-CH_2CH(CH_2CH_3)CH_2CH_2-$ and



(An)

25 If not otherwise stated, it is preferred that hydrocarbylene groups herein contain 1 to about 30 carbon atoms.

• By "substituted hydrocarbylene" herein is meant a hydrocarbylene group which contains one or more
30 substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do

not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbylene groups herein contain 1 to about 30 carbon atoms. Included within the meaning of
5 "substituted" are heteroaromatic rings.

- By " α -olefin" is meant a compound of the formula $\text{CH}_2=\text{CHR}^{19}$, wherein R^{19} is n-alkyl or branched alkyl, preferably n-alkyl.

- By "linear α -olefin" is meant a compound of
10 the formula $\text{CH}_2=\text{CHR}^{19}$, wherein R^{19} is n-alkyl. It is preferred that the linear α -olefin have 4 to 40 carbon atoms.

The product of the process described herein is an α -olefin. It is preferred that in the process a linear
15 α -olefin is produced. It is also preferred that the α -olefin contain 4 to 32, preferably 6 to 20, carbon atoms.

(I) is used as a catalyst, and a neutral Lewis acid, which is an alkyl aluminum compound of the
20 formula $\text{R}^6\text{R}^7\text{AlY}$ is also present as part of the catalyst system (sometimes called a "first compound" in the claims). It is preferred that Y is chlorine. It is also preferred that R^6 and R^7 are each independently alkyl containing 2 to 6 carbon atoms, and more
25 preferred that R^6 and R^7 are both ethyl.

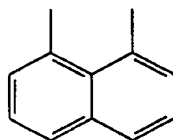
It is believed $\text{R}^6\text{R}^7\text{AlY}$ abstracts Q or S, a relatively noncoordinating anion, such as $\text{R}^6\text{R}^7\text{AlYS}^-$ is formed. It will be understood that the formulas such as $\text{R}^6\text{R}^7\text{AlYS}^-$ also includes variation in which the
30 various groups bound to aluminum may be redistributed. Relatively noncoordinating anions are known in the art, and the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-
35 1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p.

927-942 (1993), both of which are hereby included by reference.

The temperature at which the process is carried out is about -100°C to about $+200^{\circ}\text{C}$, preferably about 0°C to about 150°C , more preferably about 25°C to about 100°C . It is believed that at higher temperatures, lower molecular weight α -olefins are produced, all other factors being equal. The pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa being a suitable range. It is also believed that increasing the pressure increases the relative amount of α -olefin (as opposed to internal olefin) produced.

The process to make α -olefins may be run in a solvent (liquid), and that is preferred. The solvent may in fact be the α -olefin produced. Such a process may be started by using a deliberately added solvent which is gradually displaced as the reaction proceeds. By solvent it is not necessarily meant that any or all of the starting materials and/or products are soluble in the (liquid) solvent.

In (I) it is preferred that R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and more preferred that R^3 and R^4 are both hydrogen or methyl or R^3 and R^4 taken together are



(An)

In (I) R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl. What these groups are greatly determines whether the α -olefins of this process are made, or whether higher polymeric materials, i.e., materials

containing over 25 ethylene units, are coproduced or produced almost exclusively. If R^2 and R^5 are highly sterically hindered about the nickel atom, the tendency is to produce higher polymeric material. For instance, 5 when R^2 and R^5 are both 2,6-diisopropylphenyl mostly higher polymeric material is produced. However, when R^2 and R^5 are both phenyl, mostly the α -olefins of this process are produced. Of course this will also be influenced by other reaction conditions such as 10 temperature and pressure, as noted above. Preferred groups for R^2 and R^5 are phenyl unsubstituted in the ortho positions, and preferred groups for R^2 and R^5 are phenyl, p-methoxyphenyl, p-trifluoromethylphenyl, and p-methylphenyl.

15 Q and S are both independently anions, and both are preferably monoanions. However, Q and S taken together may also be a dianion, i.e., an anion having 2 negative charges. Useful anions for Q and/or S are chloride, bromide, alkyl, carboxylate anions, and 20 sulfonates. Preferred anions are chloride, bromide and alkyl.

As is understood by the artisan, in oligomerization reactions of ethylene to produce α -olefins, usually a mixture of such α -olefins is 25 obtained containing a series of such α -olefins differing from one another by two carbon atoms (an ethylene unit). The process for preparing α -olefins described herein produces products with a high percentage, preferably at least about 80 mole percent, 30 more preferably at least about 90 mole percent, of terminal olefinic groups (as opposed to internal olefinic groups). The product mixture also contains a relatively high percentage, preferably at least about 80 mole percent, more preferably at least about 90 mole 35 percent, of molecules which are linear. Finally relatively high catalyst efficiencies can be obtained.

Also under the correct conditions mixtures of α -olefins containing desirable numbers of carbon atoms are obtained. A measure of the molecular weights of the olefins obtained is factor K from the Schulz-Flory theory (see for instance B. Elvers, et al., Ed. Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 243-247 and 275-276. This is defined as:

$$K = n(C_{n+2} \text{ olefin}) / n(C_n \text{ olefin})$$

wherein $n(C_n \text{ olefin})$ is the number of moles of olefin containing n carbon atoms, and $n(C_{n+2} \text{ olefin})$ is the number of moles of olefin containing n+2 carbon atoms, or in other words the next higher oligomer of C_n olefin. From this can be determined the weight (mass) fractions of the various olefins in the resulting oligomeric reaction product mixture. The K factor is preferred to be in the range of about 0.6 to about 0.8 to make the α -olefins of the most commercial interest. It is also important to be able to vary this factor, so as to produce those olefins which are in demand at the moment. It has surprisingly been found that cocatalysts of the formula R^6R^7AlY give product mixtures with higher Schulz-Flory constants than alkyl aluminum compounds previously used, such as methyl alumoxane.

The α -olefins made herein may be further polymerized with other olefins to form polyolefins, especially linear low density polyethylenes, which are copolymers containing ethylene. They may also be homopolymerized. These polymers may be made by a number of known methods, such as Ziegler-Natta-type polymerization, metallocene catalyzed polymerization, and other methods, see for instance World Patent Application 96/23010, see for instance Angew. Chem., Int. Ed. Engl., vol. 34, p. 1143-1170 (1995), European Patent Application 416,815 and U.S. Patent 5,198,401

for information about metallocene-type catalysts, and J. Boor Jr., Ziegler-Natta Catalysts and Polymerizations, Academic Press, New York, 1979 and G. Allen, et al., Ed., Comprehensive Polymer Science, Vol. 4, Pergamon Press, Oxford, 1989, p. 1-108, 409-412 and 533-584, for information about Ziegler-Natta-type catalysts, and H. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, Vol. 6, John Wiley & Sons, New York, 1992, p. 383-522, for information about polyethylenes, and all of these are hereby included by reference.

The α -olefins made herein may be converted to alcohols by known processes, these alcohols being useful for a variety of applications such as intermediates for detergents or plasticizers. The α -olefins may be converted to alcohols by a variety of processes, such as the oxo process followed by hydrogenation, or by a modified single step oxo process (the 'modified Shell process'), see for instance B. Elvers, et al., Ed., Ullmann's Encyclopedia of Chemical Technology, 5th Ed., Vol. A18, VCH Verlagsgesellschaft mbH, Weinheim, 1991, p. 321-327, which is hereby included by reference.

The ethylene oligomerizations herein may also initially be carried out in the solid state by, for instance, supporting an active catalyst or catalyst precursor on a substrate such as silica or alumina. Alternatively a solution of the catalyst precursor may be exposed to a support having an alkylaluminum compound on its surface. The support may also be able to take the place of the Lewis or Bronsted acid, for instance an acidic clay such as montmorillonite. Another method of making a supported catalyst is to start a polymerization or at least make a nickel complex of another olefin or oligomer of an olefin such as cyclopentene on a support such as silica or alumina.

All of these "heterogeneous" catalysts may be used to catalyze oligomerization in the gas phase or the liquid phase. By gas phase is meant that the ethylene is transported to contact with the catalyst particle while the ethylene is in the gas phase.

In the Examples, all pressures are gauge pressures. The following abbreviations are used:

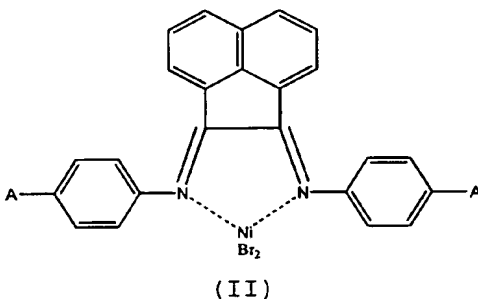
Et - ethyl

GLC - gas-liquid chromatography

MMAO - modified methyl alumoxane containing isobutyl groups, and obtained from Akzo, Inc.

Example 1 and Comparative Examples A-G

Ethylene oligomerizations were run with a nickel compound of the formula



wherein A is defined in Table 1 below.

A mechanically-stirred 1000 mL Parr® autoclave was heated overnight to 100°C under vacuum, then cooled to 30°C under an ethylene atmosphere. The autoclave was charged with 198 mL toluene via syringe, followed by Et₂AlCl (0.56 ml of a 1.8 M solution in toluene in Example 1, 2.5 ml of a 7 weight percent aluminum solution in heptane on Comparative Examples A-F, and 0.50 ml of the heptane solution in Comparative Example G). The autoclave was sealed, and ethylene was added to a pressure of 690 kPa. The solution was stirred for 15 min, and the reactor temperature set at 35°C. The ethylene pressure was then released, and a suspension of the nickel dibromide complex was added to the

autoclave via cannula. The reactor was then sealed and pressurized with ethylene to 2.8 MPa. The reaction was stirred under constant ethylene pressure for 30 min, after which time the pressure was released and the catalyst quenched with acetone and water. An aliquot of the reaction mixture was analyzed by GLC to determine the Schulz-Flory K constant. The integrated areas of the C₁₂ and C₁₄ oligomers were used to calculate the Schulz-Flory K constant. The GLC conditions used are as follows: injector and detector temperatures, 250°C; oven temperature program, 100°C/4 min, 8°C/min ramp, 250°C/70 min. The solvents were removed on a rotary evaporator, and the residual toluene was removed in vacuo overnight, leaving 4.08 g ethylene oligomers. Lower olefins lost during workup were calculated using the Schulz-Flory K constant determined from a gas chromatograph taken of the olefin products following workup which was calculated as 3.12 g in Example 1. The total oligomer mass produced for Example 1 was 7.20 g (51,000 turnovers). The olefin mixture consisted of 90% α -olefins as measured by ¹H NMR, and greater than 98 mole percent linear olefins as measured by GLC. Details of the Example and Comparative Examples are given in Table 1.

Table 1^a

Exam-ple	A	Co-Catalyst	Pressure (atm)	Time (min)	TO ^b X 10 ⁻³	mole % α -olefin ^c	Schulz-Flory K
A	CF ₃	MMAO	28	60	136	87	0.61
B	CF ₃	MMAO	56	60	113	91	0.68
C	H	MMAO	56	60	49	92	0.70
D	CH ₃	MMAO	56	60	45	91	0.71
E	OCH ₃	MMAO	28	60	114	88	0.67
F	OCH ₃	MMAO	56	60	50	95	0.74
G	CF ₃	MMAO	28	30	65	94	0.68
1	CF ₃	Et ₂ AlCl	28	30	51	90	0.81

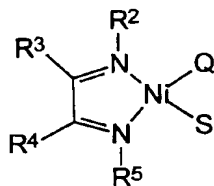
^aReaction conditions: Comparative Examples A-F, [Ni] = 1.00 X 10⁻⁴ M, 240 equivalents Al:Ni, 200 ml toluene; Comparative Example G and Example 1, [Ni] = 2.50 X 10⁻⁵ M, 200 equivalents Al:Ni, 200 ml toluene. ^bTurnover number = moles ethylene consumed/moles Ni catalyst. ^cRemainder of product are 2-alkenes.

It is clear that even though there is some variation in the Schulz-Flory constant due to variation in the structure of the α -diimine ligand in the reactions with MMAO, the change in K when using Et₂AlCl as the cocatalyst is outside the range in variation of K when the structure of the ligand is varied as shown above.

CLAIMS

What is claimed is:

1. A process for the production of α -olefins, comprising, contacting, at a temperature of about
 5 -100°C to about +200°C:
 ethylene;
 a first compound W of the formula R^6R^7AlY ; and
 a second compound of the formula

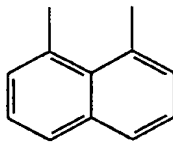


(I)

wherein:

- R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl;
 R³ and R⁴ are each independently hydrogen,
 15 hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;
 R⁶ and R⁷ are each independently alkyl;
 Y is chlorine or bromine; and
 20 Q and S are each independently an anion;
 and wherein an α -olefin containing 4 to 40 carbon atoms is produced.
2. The process as recited in claim 1 wherein Y is chlorine, and R⁶ and R⁷ are each independently alkyl
 25 containing 2 to 6 carbon atoms.
3. The process as recited in claim 2 wherein both R⁶ and R⁷ are ethyl.
4. The process as recited in claim 2 wherein R³ and R⁴ are each independently hydrogen or hydrocarbyl,
 30 or R³ and R⁴ taken together are hydrocarbylene to form a ring.

5. The process as recited in claim 4 wherein R^3 and R^4 are both hydrogen or methyl or R^3 and R^4 taken together are



5 6. The process as recited in claim 1 wherein R^2 and R^5 are phenyl or substituted phenyl in which the ortho positions are unsubstituted.

7. The process as recited in claim 5 wherein R^2 and R^5 are phenyl or substituted phenyl in which the
10 ortho positions are unsubstituted.

8. The process as recited in claim 1 wherein R^2 and R^5 are phenyl, p-methoxyphenyl, p-trifluoromethylphenyl, or p-methylphenyl.

9. The process as recited in claim 7 wherein R^2
15 and R^5 are phenyl, p-methoxyphenyl, p-trifluoromethylphenyl, or p-methylphenyl.

10. The process as recited in claim 1 wherein said temperature is about 25°C to about 100°C.

11. The process as recited in claim 1 wherein Q
20 and S are selected from the group consisting of chloride, bromide and alkyl.

12. The process as recited in claim 4 wherein Q and S are selected from the group consisting of chloride, bromide and alkyl.

25 13. The process as recited in claim 7 wherein Q and S are selected from the group consisting of chloride, bromide and alkyl.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/18708

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C2/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 23010 A (E. I. DU PONT DE NEMOURS; UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL) 1 August 1996 (1996-08-01) cited in the application claims 439-450 -----	1-13

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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22/11/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/18708

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